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THE PRODUCTION OF ATOMS AND SIMPLE RADICALS IN GLOW DISCHARGES

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I. INTRODUCTION

The size and topical variety of this symposium clearly show that electrical discharges are finding increasing application in many areas of chemistry ranging from the production of simple atomic species such as H, O, or N from their diatomic molecules to the synthesis or specific decomposition of complex organic or inorganic compounds. It is unfortunately true that our understanding of the chemistry of discharge processes is still in a rudimentary state, that the field is more an art than a science, and thus represents one of the last frontiers of chemistry.

There is good reason for this unsatisfactory state of affairs. Glow discharges are complex phenomena in which gases at sub-atmospheric pressure are undergoing excitation and ionization by electron impact and so give rise to highly unequilibrated steady-state conditions where the effective temperature of free electrons is typically tens of thousands °K, that of electronically or vibrationally excited states may be thousands of °K, whereas the translational and rotational temperature will only be tens to hundreds of °K above ambient. It should be clear, of course, that apart from the processes occurring at the electrodes, energy from the electric field is coupled to the gas almost entirely through the kinetic energy of free electrons which, due to their small mass, acquire energy rapidly from the field, lose it negligibly slowly in elastic collisions (the mean fractional energy loss per elastic collision equals $2 m/M$ in the simplest classical model where m and M are the masses of the electron and of the molecule), and thus reach their steady-state distribution through various inelastic processes. In this manner, electrons become sufficiently energetic to

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ionize some of the neutral species and thereby balance their continuous loss by diffusion, attachment, and recombination. As the ionization potentials of most neutral gases are in the 10 to 20 ev range (230 to 460 kcal/mole), an appreciably fraction of the electrons has enough energy to produce electronic excitation (responsible for the emitted glow) and dissociation.

In the following sections, the mechanism of dc and ac glow discharges will be briefly described, with emphasis on high frequency electrodeless discharges ($f = 10^6$ to 10^{10} sec⁻¹) and on the simple geometry often encountered in rapidly pumped steady-state flow systems at pressures near 1 torr. After a brief discussion of the rates and energy dependence of specific collision and diffusion processes, available experimental data will be brought to bear on the problem of H₂, N₂, and O₂ dissociation and of the chemistry of some more complicated systems.

Although there are several fine monographs available on electron impact phenomena and discharge physics¹⁻⁴, they contain relatively little information on active high frequency discharges which is pertinent to the problem of dissociation and chemical reaction. The electron physics of microwave discharges is discussed in some review articles.^{5,6}

II. BASIC PHYSICAL PROCESSES

II. 1. General Mechanism and Frequency Dependence.

Glow discharges are typically observed in the pressure range of about 0.1 to 10 torr. At much lower pressures, the electron mean free path is too long for gas collisions to be important, electrons pick up large amounts of energy from the dc or slow ac field and bombard the anode or the tube wall which may then fluoresce. At much higher pressures, the mean free path is very short, the breakdown field strength is very high, and when it is exceeded, local, highly ionized, but narrow pathways are created for the conduction of current, i.e. spark

filaments are formed. The normal dc glow discharge in a long cylindrical tube is characterized by many axially distinct but radially fairly uniform regions of quite different optical and electrical properties such as the Aston Dark Space, Cathode Glow, Cathode Dark Space, Negative Glow, Faraday Dark Space, Positive Column, Anode Glow, and Anode Dark Space, in this order, between cathode and anode. The reason for this complexity is that quite different processes occur in the different regions as is also shown by a very non-uniform voltage rise between cathode and anode. Most of the potential difference is taken up in the 'cathode fall' which comprises the first four regions enumerated above, is dependent on the cathode material as well as on the nature of the gas and on the natural variable E/N ($V\text{ cm}^2/\text{molecules}$) where E is the field strength (V/cm) and N the total neutral density ($\text{molecules}/\text{cm}^3$). The 'cathode fall' and 'anode fall' regions also have large gradients of electron and ion concentrations and a local imbalance of electrical charge. The positive column is simpler in nature (although striated positive columns are still poorly understood), has a small and constant axial voltage drop, and only a small imbalance of charge carriers, because, although electrons initially diffuse to the tube wall faster than ions, the resultant radial field prevents further charge separation and forces electrons and ions to diffuse equally fast. This process is called ambipolar diffusion and is further discussed below. The quantity E/N is a measure of the electron energy under conditions of steady-state drift, and takes on a well-defined, constant value in the positive column. To obtain a simple expression relating the electron energy, $\epsilon = \frac{1}{2} m\bar{v}^2$, to E/N , we equate energy loss and gain per electron per second, $\frac{2m}{M} \frac{\epsilon \bar{v}}{\ell} = eEw$, where ℓ is the mean free path for electron-neutral collisions, e the electronic charge, and $w = \frac{2}{3} \frac{eE\ell}{m\bar{v}}$ the electron drift velocity. One obtains $\epsilon = \frac{E}{N} \frac{eM^{1/2}}{2\pi\sigma^2(3m)^{1/2}}$ where ℓ was replaced by $1/(2^{1/2}\pi\sigma^2N)$ from simple kinetic theory.

The voltage drop along the positive column is also independent of the

total current over a fairly wide range, and since the current, i , is carried mostly by the electrons whose drift velocity is about 100 times larger than that of the ions, $i = n_e e v = \frac{2}{3} \frac{e^2 E \ell}{m \bar{v}} n_e$, which shows that the electron concentration, n_e , increases linearly with increasing current because E and \bar{v} are constant. In its normal range of electron (and ion) concentrations of 10^8 to 10^{11} cm^{-3} , the positive column of a dc glow discharge is diffusion-controlled and serves as the electrical connection between the cathode and anode regions.

In high frequency electrodeless discharges the complications of the cathode and anode regions are absent, the entire plasma is approximately neutral and diffusion-controlled, and the discharge often resembles the positive column of an equivalent dc discharge. Yet, there are differences in its fundamental mechanism, especially at microwave frequencies. Free electrons oscillating in an alternating field can not derive power from the field on the average, because their motion is 90° out of phase with the field. They therefore acquire energy only because collisions with neutral molecules change their phase relationship with the field, while at the same time representing a small fractional loss of the energy gained. Under the assumption that the ac frequency, f , is greater than the elastic collision frequency, ν_e , the maximum displacement, x , of an electron due to the high frequency field is given by $x = \frac{2eE}{m\omega^2}$ where $\omega = 2\pi f$. In an active microwave discharge E is typically 30 V/cm and x is therefore less than 10^{-3} cm when $f = 2.5 \times 10^9 \text{ sec}^{-1}$ (as in the widely used Raytheon Microtherm Generator). The corresponding maximum electron energy acquired during the cycle is eEx , about 0.02 ev, i.e. the electrons slowly accumulate the energy necessary to undergo inelastic, ionizing collisions and to sustain the discharge. When elastic collisions are approximately accounted for, it is convenient to define an effective field strength, $E_e = E_0 \left(\frac{\nu^2}{\nu^2 + \omega^2} \right)^{1/2}$ where E_0 is the rms value of the applied field strength. The power gained from the field per electron is $\frac{e^2 E_e^2}{m\nu}$ and per collision therefore $\frac{e^2 E_e^2}{m\nu^2}$.

II. 2. Diffusion of Charged Species.

In the discharges of interest here, the concentration of charged species is greater than 10^8 cm^{-3} and a large fractional separation of electrons and positive ions becomes impossible, because it would set up a very large opposing field. The currents of electrons and ions reaching the wall must then be equal, $i_e = -D_e \nabla n - n \mu_e E'$, $i_+ = -D_+ \nabla n + n \mu_+ E'$ where $n = n_e = n_+$ is the electron density, ∇n the density gradient, D the diffusion coefficient, μ the mobility, and E' the field due to the (small) space charge. The subscripts e and $+$ refer to electron and positive ion. Equating i_e and i_+ and eliminating E' one obtains

$$i = - \frac{D_e \mu_+ + D_+ \mu_e}{\mu_+ + \mu_e} \nabla n = D_a \nabla n$$

which serves as the definition of the ambipolar diffusion coefficient, D_a . Substituting $\mu_e \frac{kT_e}{e}$ for D_e and the equivalent expression for D_+ one obtains

$$D_a = \frac{\mu_e \mu_+}{\mu_e + \mu_+} \frac{k}{e} (T_e + T_+)$$

which approximately equals $\frac{\mu_+ k}{e} (T_e + T_+)$ or $D_+ (1 + \frac{T_e}{T_+})$ because the electron mobility μ_e , is much larger than the ionic mobility μ_+ . In active glow discharges T_e/T_+ is typically 20 to 100, whereas in the afterglow the electrons thermalize rapidly and $T_e/T_+ = 1$. Thus, $D_a \approx 20$ to $100 D_+$ in the active discharge, and $2 D_+$ in the afterglow.

The disappearance of charged species by ambipolar diffusion in the absence of a source term is described by the diffusion equation $\frac{\delta n}{\delta t} = D_a \nabla^2 n$ where n is a function of r , θ , z , and t . The well-known solution of this equation for the case of an infinite cylinder is $n(r, t) = \sum_{i=1}^{\infty} A_i J_0(\alpha_i \frac{r}{r_0}) e^{-k_i t}$ where α_i is the i th root of J_0 , the Bessel function of zero order and $k_i = (\frac{\alpha_i}{r_0})^2 D_a = \frac{D_a}{\Lambda^2}$. The diffusion length, Λ , therefore equals $\frac{r_0}{\alpha_1}$. The first few zeroes of J_0 are $\alpha_1 = 2.405$, $\alpha_2 = 5.520$, $\alpha_3 = 8.654$, $\alpha_4 = 11.792$ which shows that, as diffusion proceeds, the time decay will be increasingly governed by $k_1 = (\frac{2.405}{r_0})^2 D_a$, the

first (lowest) diffusion mode, because the next three higher modes are damped out more rapidly by factors of 5.3, 12.9, and 24. After a short transient, the diffusion-controlled electron decay or the diffusion controlled loss under steady-state conditions with a spatially well distributed source term can therefore be closely approximated by a first-order rate constant, $k = 5.78 D_a / r_o^2$.

This analysis applies when there are only positive ions and electrons present. When negative ions are also present, their principal effect is to accelerate the ambipolar diffusion of the electrons, $(D_a)_e$, which now becomes approximately $(D_a)_e = (1 + \lambda) D_+ (1 + \frac{T_e}{T_+}) + \lambda D_- (\frac{T_e}{T_+} - 1)$ which for active discharges ($T_e/T_+ \gg 1$) can be further approximated by $(1 + 2\lambda) T_e/T_+$, where $\lambda = n_-/n_e$, the concentration ratio of negative ions and electrons. It can be seen that for $\lambda > 1$ electrons will be lost much more rapidly by diffusion to the wall than in the absence of negative ions.

II. 3. Electron-Ion and Ion-Ion Recombination.

Although several radiative, two-body, and three-body recombination mechanisms exist, only the fastest ones will be mentioned here. These are the dissociative recombination of electrons and positive molecular ions as exemplified by $NO^+ + e \rightarrow N + O$ (where the products are likely to be electronically excited), similar ion-ion reactions such as $I_2^+ + I^- \rightarrow I_2 + I$ or $3I$, $NO^+ + NO_2^- \rightarrow$ neutral products, and three-body ion-ion recombinations such as $NO^+ + NO_2^- + M \rightarrow$ neutral products.

All of these processes have very large rate constants, due to the long range coulombic attraction between reactants, if reasonable paths are available for the dissipation of the large exothermic reaction energy (~ 10 ev) such as dissociation and electronic excitation. The first of these three processes has been studied in greatest detail, especially by Biondi and coworkers^{7,8} who found a value of $2.9 \pm 0.3 \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for the rate constant of

$N_2^+ + e \rightarrow N + N$, for example. The generally observed range of 1 to 5×10^{-7} (6×10^{13} to 3×10^{14} lit mole $^{-1}$ sec $^{-1}$) means that at an electron and ion concentration 10^{11} cm $^{-3}$, which is near the upper limit of charged particle densities encountered in glow discharges, the effective first order rate constant for electron removal under steady-state conditions will be 1 to 5×10^4 sec $^{-1}$.

Two-body ion-ion recombinations have rate constants in the same general range, although few have been studied in detail, none with precise analysis of reactants and products. Some three-body ion-ion recombinations have recently been studied by Mahan and coworkers^{9,10} who found effective termolecular rate constants in the range 4×10^{-26} to 3×10^{-25} cm 6 molecule $^{-2}$ sec $^{-1}$ for $NO^+ + NO_2^- + M$ near 300°K. With an approximate $T^{-5/2}$ dependence, and at a total pressure of 1 torr, such processes would have effective first-order rate constants of ion removal in the 10 to 100 sec $^{-1}$ range, too slow to be of importance.

II. 4. Electron Attachment and Detachment.

Only the fastest of the many possible processes need to be discussed here. Radiative attachment and photodetachment as well as three-body attachment processes are unlikely to be of importance. Dissociative attachment reactions such as $e + O_2 \rightarrow O^- + O$ have rate constants¹¹ which rise from zero at an electron energy threshold (4 to 9 ev for the formation of O^- from O_2 , NO, or CO) to a maximum of 10^{-11} to 10^{-10} cm 3 molecule $^{-1}$ sec $^{-1}$ for electrons with 6 to 10 ev. For average electron energies of 2 to 3 ev in an active discharge, the effective rate constant must therefore be lowered about 10 fold to a range of 10^{-12} to 10^{-11} . Moreover, several associative detachment reactions such as $O^- + O \rightarrow O_2 + e$, $O^- + N \rightarrow NO + e$, $O^- + H_2 \rightarrow H_2O + e$ have recently been found¹² to be very rapid ($k = 1$ to 5×10^{-10} cm 3 molecule $^{-1}$ sec $^{-1}$) under thermal conditions near 300°K. This further reduces the likelihood that negative ions are important species in rapidly pumped steady-state glow discharges of diatomic

gases. In this regard, active discharges probably differ markedly from their corresponding afterglows or from drift tube experiments where electron attachment or secondary negative ion reactions produce various negative ions of low electron affinities.

II. 5. Charge-Transfer and Ion-Molecule Reactions.

Both positive and negative ion-molecule reactions have recently been studied by a variety of experimental methods, and consistent values for many rate constants have become available. Because of the strong ion-dipole or ion-induced dipole interaction, these reactions usually have little or no activation energy if they are exothermic, and often have rate constants near $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, in accord with the simple theory based on the polarizability of the neutral reactant. Some exceptions such as $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$ which is at least 10^6 times slower are probably due the large energy requirements for bond rearrangement which in the corresponding neutral four-center reaction gives rise to a very large activation energy. Other unusually slow reactions such as $\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$ ($k \sim 2 \times 10^{-12}$) are less easily rationalized, particularly since k rises sharply when the reactant N_2 is vibrationally excited.

From the magnitude of 10^{-10} to 10^{-9} for many of the exothermic reactions it is clear that the effective first-order rate constant for the transformation of an ionic species by reaction with a major neutral constituent ($P = 1 \text{ torr} = 2 \times 10^{16} \text{ molecules cm}^{-3}$ at the higher temperature of the discharge) is 2×10^6 to $2 \times 10^7 \text{ sec}^{-1}$, i.e. such reactions will go to completion in a small fraction of the residence time in even the most rapidly pumped flow systems. Minor neutral constituents such as atomic species at 0.1 to 1 more % will transform ionic species with rate constants of 10^3 to 10^5 sec^{-1} , still much faster than the rate of traversal through most discharges whose average flow velocities are in the range 10^2 to 10^4 cm sec^{-1} and whose lengths are 1 to 10 cm.

II. 6. Electron Impact Ionization.

As shown in section II. 2 above, the electron loss term by ambipolar diffusion can be approximated by a first-order rate constant, $k = 5.78 D_a / r_o^2$, which for an active discharge with $T_e / T_+ \sim 50$, $D_+ \sim 100 \text{ cm}^2/\text{sec}$, and $r_o = 0.5 \text{ cm}$, makes $k \sim 1 \times 10^5 \text{ sec}^{-1}$. Although it is conceivable that chemi-ionization will occur in which two electronically excited molecules with 5 to 10 ev energy react to produce ionization, such processes will normally be of very minor importance. Even with a very large chemiionization rate constant of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, a concentration of $5 \times 10^{14} \text{ cm}^{-3}$, 2 to 3 mole %, of such excited molecules would be required to balance the diffusional loss. It thus seems likely that electron impact ionization is the major source term for charged species in the discharge. Although this requires more than the ionization potential of the atom or molecule, i.e. electron energies in excess of about 15 ev, the large electron velocity and its very high average temperature, T_e , can easily provide the required magnitude of the rate constant.

The ionization cross section of most atoms and simple molecules rises sharply from zero at the ionization potential and comes to a broad maximum of about $1 \text{ to } 5 \times 10^{-16} \text{ cm}^2/\text{molecule}$ at electron energies of 70 to 120 ev. It normally reaches a value of 1×10^{-17} about 2 to 4 ev above its ionization potential, i.e. at electron energies of 12 to 17 ev. For average electron energies of 2 to 3 ev in active glow discharges, this leads to total effective ionization rate constants of $10^{-11} \text{ to } 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ if a Maxwell distribution is assumed. A somewhat lower range would be obtained for a Druyvesteyn distribution, but since the ratio, $\epsilon/\bar{\epsilon}$, of required to average energy is never very large, the error due to the assumption of a Maxwell distribution should be fairly small.

An important, though infrequently applicable ionization mechanism is the direct ionization by collision with sufficiently energetic, metastable

neutral species. This process, called Penning ionization, can occur only if the excitation energy of the metastable exceeds the ionization potential of the other reactant. For He, Ne, and Ar the excitation energy of the lowest triplet state is 19.80, 16.62, and 11.55 eV respectively, and since the rate constants for Penning reactions are often gas kinetic, i.e. near $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, this process is likely to be the major ionization source in diatomic gases mixed with excess He or Ne but not with Ar.

II. 7. Excitation and Dissociation

Molecules can have internal energy in the form of rotation, vibration, or electronic excitation, and they can therefore undergo inelastic collisions with electrons which leave the molecule in one of its many excited states. For the purpose of this review, rotational excitation need not be considered, because rotational energies are small, and the collisional exchange of translational and rotational energy is so rapid that rotational states are unlikely to be substantially out of kinetic temperature equilibrium. Vibration-translation interchange, however, is very inefficient, especially for strongly bound, homonuclear diatomic molecules, so that appreciable vibrational excitation can occur in glow discharges, and effective vibrational temperatures may be established which are intermediate between T_e and T_g . Electron impact excitation of vibrational energy is a highly specific process whose cross section can differ by two orders of magnitude from one molecule to another, because it depends on the existence of virtual negative ion states which decay into vibrationally excited ground-state molecules and slow electrons. This mechanism is particularly important in N_2 , CO, and CO_2 which have large cross sections ($1 \text{ to } 5 \times 10^{-16} \text{ cm}^2/\text{molecule}$, $k = 5 \times 10^{-9} \text{ to } 2 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at electron energies of about 2 to 5 eV), but less so in H_2 and O_2 whose cross sections are a factor of 10 to 50 smaller than those in N_2 . The high vibrational temperature, T_v , of N_2 in glow discharges is likely to be responsible for much of its electronic excitation, because if T_v approaches T_e ,

the internal equilibration of vibrational states will produce appreciable concentrations of molecules with 5 to 8 ev of vibrational energy, consistent with some recent spectroscopic observations in active nitrogen¹³ as well as electronically excited molecules by the reverse process of the very fast quenching reactions of the $A^3\Sigma$ state of N_2 by N-atoms.

Electronically excited states can be formed directly by electron impact. When the corresponding radiative transition is allowed, the excitation cross section rises to a broad maximum and then slowly decreases, whereas for forbidden radiative transitions, the cross section is often sharply peaked at the corresponding energy and falls off rapidly at higher energies. Peak cross sections are often in the 10^{-17} to 10^{-16} $\text{cm}^2/\text{molecule}$ range which roughly corresponds to rate constants of 10^{-11} to 10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for transitions requiring 5 to 10 ev, assuming average electrons energies of 2 to 3 ev.

The principal mechanism for the direct dissociation of a molecule into neutral fragments by electron impact must, of course, be the initial formation of an electronic state with energy greater than D, the dissociation energy. This transition will take place within the limitations set by the Franck-Condon principle. The ensuing dissociation will normally come about in one of three principal ways: (a) the upper state is repulsive and dissociates upon its first pseudovibration, i.e. in about 10^{-13} sec; (b) the upper state is bound, but the molecule is formed on the repulsive part of its potential energy curve at a point above its dissociation energy, and will therefore dissociate on its first vibration, also in about 10^{-13} sec; (c) the upper state is bound, the molecule is formed with less than the dissociation energy of that state, but there is another state of lower dissociation energy with which the first state may interact. Near the crossing point of the two potential energy curves, the states become mixed and there is a probability of crossing and subsequent dissociation. Depending on the degree of mixing, this predissociation process may be very much slower than the first two. The overall cross section and rate constant for dissociation will

normally equal that of the primary excitation step, i.e. there will be near unit probability for the subsequent dissociation, because collisional or radiative lifetimes of the excited states can not be shorter than about 10^{-7} to 10^{-8} seconds.

III. APPLICATION TO THE DISSOCIATION OF SOME DIATOMIC MOLECULES.

III. 1. Summary of Some Atom Production and Loss Processes

In the following sections much evidence will be cited for catalytic effects in the production of atomic species such as H, N, or O in glow discharges of their diatomic gases. The existence of such effects suggests large changes in the atom production or loss terms upon small variations in gas composition. The principal processes are therefore summarized in this section, and approximate ranges given for their rates. A cylindrical discharge tube of 1 cm diameter, average electron concentration of 10^{11} cm^{-3} , and electron energy of 2 to 3 ev are assumed corresponding to known conditions in microwave discharges¹⁶ at input power levels of about 10 to 500 watt.

Production terms: (a) Electron impact dissociation via excited states depends on the existence of a dissociating or predissociating state at moderate excitation energy and is therefore quite variable. When the dissociation energy is relatively small, as in H and O, and when states are available at 8 to 10 ev excitation threshold, an atom production rate of 10 to 100 torr/sec can be calculated. For N_2 whose dissociation energy is larger, the rate will be at least 10 times lower. It should be clear that this process must occur in active discharges, since electron impact ionization, which requires appreciably larger electron energies, is the principal source term for electron production. Therefore, since there are enough electrons present with 15 to 20 ev energy to balance the rapid ambipolar diffusion (and recombination) loss, there must be appreciably more with 8 to 12 ev for excitation-dissociation.

(b) Electron-Ion recombination at the wall (following ambipolar diffusion) or in the gas phase will also produce atomic species in reactions such as

$e + H_2^+ \rightarrow 2 H$, $e + N_2^+ \rightarrow N + N$, etc. It is clear that the upper limit to this atom production term is given by the total rate of ionization except for a possible factor of two from the stoichiometry of the dissociation. But as this surface recombination may also lead to the molecular product by the dissipation of energy to the surface, the dissociation rate due to this process is likely to be lower than the corresponding ionization or equivalent ambipolar diffusion term, i.e. < 0.5 to 5 Torr/sec. The gas-phase dissociative recombination will produce atoms at a rate of 0.1 to 0.3 Torr/sec at an electron density of 10^{11} cm^{-3} and much more slowly at lower densities.

(c) Ion-molecule reactions of primary ions may in exceptional cases be sufficiently exothermic to produce atomic species and ions of lower ionization potential such as in $H_2^+ + H_2 \rightarrow H_3^+ + H$, but the equivalent reactions for O_2 and N_2 are endothermic. When such a process is possible, its rate is again limited by the total rate of ionization, but should closely approach it if the neutral molecule is a major species as in the above H_2 reaction.

(d) Neutral-neutral dissociation reactions may also occur, but little can be said about them in general. As the kinetic temperature of all but the electrons is fairly low (300 to 800°K , mostly near 600°K), two excited, metastable molecules would have to react to transfer their excitation to a predissociating state. Few such reactions are known, and their rate constants are likely to have upper limits in the 10^{-12} to $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ range. If that were so, metastable mole fractions as high as 0.1% would only produce atoms at ratios of 0.02 to 0.2 Torr/sec. Such states would also have to be optically metastable, i.e. have radiative lifetimes longer than 0.01 sec, and be resistant to collisional quenching, i.e. have deactivation probability per collision lower than 10^{-4} .

Loss Terms: (a) Homogeneous gas-phase atom recombinations are three-body processes with rate constants near $10^{-32} \text{ cm}^6 \text{ molecule}^{-1} \text{ sec}^{-1}$ so that even for atom mole fractions of 5% , such loss rates are near 0.01 torr/sec, negligibly

small.

(b) Surface recombination is a well-known process, usually kinetically first order, and characterized by a rate constant, $k = \frac{\gamma \bar{c}}{d}$, for a cylindrical tube of diameter d . Here γ is the recombination coefficient, the fraction of surface collisions leading to recombination, and \bar{c} is the average molecular velocity of the atomic species. γ which is often as low as 10^{-5} outside the discharge for a well-cleaned or suitable poisoned surface, is likely to be 10^{-3} or larger in the active discharge. For $\gamma = 10^{-3}$, atom loss rates of 2 to 10 torr/sec can be calculated, and for larger γ , these rates would be larger, but not proportionately so, because large radial concentration gradients would be produced and diffusion would become rate-controlling. Then, an effective first order rate constant, $k = D/\Lambda^2 = 5.8 D/r^2$, would be applicable, similar to ambipolar diffusion (Section II.2), but with the smaller, molecular diffusion coefficient. For an atom mole fraction of 5%, the upper limit to the diffusional atom recombination rate will be 100 to 300 torr/sec depending on the atomic species.

(c) Ion-molecule reactions can remove atomic species if the ion is polyatomic such as in $N + N_3^+ \rightarrow N_2 + N_2^+$ or the equivalent oxygen reaction. If the polyatomic ion is a major ionic species, and the reaction is a fast one, its rate at 5% atom mole fraction will be near 5 torr/sec. It will then be limited by the rate of regeneration of the polyatomic ion. Reactions of the type $O_2^+ + N \rightarrow NO^+ + O$ or $N_2^+ + O \rightarrow NO^+ + N$ are known to be fast, but as they replace one atomic species by another they need not be considered here.

(d) Neutral, bimolecular atom-molecule reactions such as $N + O_2 \rightarrow NO + O$ or $O + H_2 \rightarrow OH + H$ often have appreciable activation energies. Moreover, they, too, only shuffle atomic species and can not be considered loss terms. In the few applicable cases where this does not hold as in $O + N_2O \rightarrow 2 NO$ or $N + N_2O \rightarrow N_2 + NO$, the reactions are known to be negligibly slow.

III. 2. Hydrogen Discharges

The discussion of the electron collisional aspects of H_2 , N_2 , and O_2 discharges is greatly aided by the excellent papers by Phelps and coworkers in which elastic and inelastic collision cross sections are obtained by numerical solution of the Boltzmann transport equation and comparison with all available experimental data on electron transport coefficients. For H_2 and D_2 ¹⁴, the effective vibrational excitation cross section becomes appreciable (10^{-17} cm^2) at about 1 ev and peaks near 5 ev at $8 \times 10^{-17} \text{ cm}^2$. For dissociation, a threshold at 8.85 ev and peak of $4.5 \times 10^{-17} \text{ cm}^2$ at 16 to 17 ev was found to be consistent with the data. A recent measurement by Corrigan¹⁵ of the dissociation cross section of H_2 is in good agreement with the above except for a larger peak of about $9 \times 10^{-17} \text{ cm}^2$ at 16.5 ev. For average electron energies, ϵ_k , of 3.0 or 2.0 ev¹⁶, dissociation rate constants, k_d , of 11 or $2 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$ can be calculated by summation of $Qv f(\epsilon)$ from $\epsilon = 0$ to ∞ , using energy increments of 2 or 3 ev, where Q is the appropriate cross section, v the electron velocity, and

$$f(\epsilon) = \frac{2}{\pi^{1/2}} \left(\frac{\epsilon}{\epsilon_k} \right)^{1/2} e^{-\frac{\epsilon}{\epsilon_k}} \frac{d\epsilon}{\epsilon_k}$$

is the Maxwell distribution function. Such k_d 's correspond to H-atom production rates of 200 or 40 torr/sec. An effective ionization rate constant, k_i , was similarly found to be 7×10^{-11} ($\epsilon_k = 3 \text{ ev}$) or 6×10^{-12} ($\epsilon_k = 2 \text{ ev}$), corresponding to ionization rates of 7 or 0.6 torr/sec, respectively. The latter should be approximately equal to the ambipolar diffusion loss, $5.8/r_0^2 D_+ T_e n_e / T_g$, which equals 9 or 6 torr/sec if $D_+ = 700 \text{ cm}^2/\text{sec}$ at 1 torr pressure. This crude calculation suggests that $\epsilon_k = 3 \text{ ev}$ is a better choice than 2.0 ev. It neglects the serious deviation from a Maxwell distribution which is to be expected.

More realistic estimates of k_d and k_i were obtained by Dr. Phelps by simultaneously adjusting E/N , ϵ_k , and using the appropriate rate coefficients

to balance ionization against diffusion losses. This led to values of $\epsilon_k = 3.0 \text{ ev}$,^{*} $E/N = 1.1 \times 10^{-15} \text{ V cm}^2/\text{molecule}$ and $k_i = 7 \times 10^{-11}$, in surprising agreement with the above. With that E/N , an estimate of k_d can be obtained from ref. 14, Fig. 8 by multiplying the excitation coefficient ($8 \times 10^{-17} \text{ cm}^2/\text{molecule}$) by the drift velocity ($1.5 \times 10^7 \text{ cm/sec}$) which gives $k_d = 1.2 \times 10^{-9}$, also in fortuitously good agreement with 1.1×10^{-9} above. This excitation coefficient includes other, non-dissociating processes, but since application of Corrigan's¹⁵ larger dissociation cross section would increase the total excitation coefficient, its subsequent apportioning would not lead to serious discrepancies.^{**}

Thus, a very large atom production term of about 200 torr/sec is indicated by all available estimates. In addition, there is the source term due to electron-ion recombination at the wall, and due to the fast reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. Each of these can at most equal the ionization rate, so that their sum will contribute 10 to 20 torr/sec of atomic hydrogen. All other source terms are negligible.

Surface recombination provides the only comparably large loss term in the discharge. For small γ , the first order rate constant, $k_s = \gamma \bar{c}/d = 2 \times 10^5 \gamma$, and the steady-state atom concentration, $[\text{H}]_{ss}$ is approximately $1 \times 10^{-3}/\gamma$. This shows that γ must always be relatively large, and that the diffusion controlled $k_s = 5.8 D/r^2 = 2$ to $4 \times 10^4 \text{ sec}^{-1}$ may be applicable which leads to an $(\text{H})_{ss}$ of 0.5 to 1×10^{-2} torr, less than 1% mole fraction. When γ is lowered to 10^{-2} , $[\text{H}]_{ss} = 0.1$ torr, and under either condition the halflife for this formation is very short (3×10^{-5} or 3×10^{-4} sec).

One is thus led to the interesting conclusion that the dissociation yield of such H_2 discharges is mainly controlled by surface recombination and that the surface in the discharge must be moderately to highly efficient for

* The quantity ϵ_k is here defined to equal eD/μ , the ratio of diffusion coefficient to mobility. It is an experimentally determined measure of the electron energy even when the energy distribution is not maxwellian.

** It is Dr. Phelps's view that the high E/N portion of the enelastic collision frequency and the corresponding cross sections will have to be modified in view of recent work by Fletcher and Haydon, Austral. J. Phys. 19, 615 (1966).

atom recombination. Moreover, the effect of small amounts of added gases such as H_2O or O_2 in increasing the yield must be through their influence on the surface efficiency, as they can not affect the principal production term and as no homogeneous loss mechanisms of proper magnitude are available. These conclusions are in general agreement with recent work by Goodyear and Von Engel¹⁷ on radio frequency discharges at lower pressure and of different geometry.

The very large body of experimental work on the "catalytic" production of H when small amounts of H_2O or O_2 are added will not be reviewed here. The effect is unquestionably real, i.e. factors of 10 or so in H-atom yield when switching from "dry" H_2 to H_2 containing 0.1 to 0.3% H_2O can be demonstrated routinely and reversibly. Rony and Hanson¹⁸ have recently questioned the existence of such an effect at a pressure of 0.075 torr and have reviewed the general subject. Our early experiments do not bear this out, as they show a large catalytic effect for added H_2O , but they do indicate that the effect is less pronounced at pressures below 0.1 torr. This trend can be expected if the above analysis is correct, because at low pressures, the production terms are decreased and the loss terms increased. Moreover, for a given discharge energy input, the surface should be hotter at low pressure, and this may nullify the deactivation which is probably due to adsorbed water molecules. Several of the relevant experiments are now under way in our laboratory by Dr. D. A. Parkes, using Lyman- α absorption for the downstream measurement of [H].

III. 3. Oxygen Discharges

Electron collision cross sections have been calculated by Hake and Phelps¹⁹ from all available experimental data on electron drift velocity and other transport coefficients. The cross sections for vibrational excitation are much smaller than in H_2 and that process can probably be neglected. Electronic excitation is described by three processes with thresholds at 4.5, 8.0, and 9.7 ev. The latter two are larger than the first, and should lead to dissociation, since the upper

states have shallow potential energy minima at larger internuclear distances than the ground state. The combined cross section for the 8.0 and 9.7 ev excitation shows a broad first peak of $1.1 \times 10^{-16} \text{ cm}^2$ at 12 to 15 ev, then drops slightly and rises again to a second peak in the 50 to 100 ev range. With the assumption of an average electron energy, ϵ_k , of 3.0 ev the effective dissociation rate constant, k_d , is about $2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

The corresponding ionization rate constant, k_i , was calculated to be $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Fitting the O_2 data in a similar way to H_2 , Dr. Phelps obtained $E/N = 9 \times 10^{-16} \text{ V cm}^2/\text{molecule}$, $\epsilon_k = 3.4 \text{ ev}$, $k_d = 1 \times 10^{-9}$, and $k_i = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, in fair agreement with the above except for the smaller k_i , but k_i is strongly dependent on E/N near $10^{-15} \text{ Vcm}^2/\text{molecule}$, so that a 20% increase of E/N would lead to a tenfold increase of k_i .

An O-atom production rate of about 200 torr/sec by dissociative electron impact is thus indicated, and all other production terms are negligible by comparison. Surface recombination of O-atoms is kinetically similar to that of H-atoms except for a lower diffusion coefficient and molecular velocity by a factor of 3. Thus, the effective first order surface recombination rate constant is $6 \times 10^4 \gamma \text{ sec}^{-1}$ for small γ and $5 \times 10^3 \text{ sec}^{-1}$ for γ approaching unity.

In pure O_2 , as in N_2 , there is another loss term which does not arise in H_2 . The polyatomic ions O_3^+ and O_4^+ can react exothermically and rapidly via $\text{O}_4^+ + \text{O} \rightarrow \text{O}_3^+ + \text{O} \rightarrow \text{O}_2^+ + \text{O}_2$ to recombine O-atoms. To obtain an upper limit for this loss rate one may assume that O_4^+ is a major ion, i.e. $[\text{O}_4^+] = 10^{11} \text{ cm}^{-3}$, and that it is therefore regenerated by the bimolecular reaction $\text{O}_2 + \text{O}_2^+ \rightarrow \text{O}_4^+$. The latter assumption requires that the lifetime of the unstabilized O_4^+ collision complex be equal to or longer than the collision time, $3 \times 10^{-7} \text{ sec}$, which seems excessively long for such a simple species. At its (unreasonable) maximum estimate, such a chain process may recombine O-atoms at twice the rate of $\text{O}_4^+ + \text{O} \rightarrow \text{O}_3^+ + \text{O}_2$, i.e. with an effective first order rate constant of 200 sec^{-1} if both ion molecule reactions have rate constants of

$10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Even so, it would not seriously limit O-atom production, since the corresponding $[O]_{ss} = 0.5 \text{ torr} = 50\% \text{ mole fraction}$. Moreover, Knewstubb, Dawson, and Tickner²⁰ saw no O_4^+ in their mass-spectrometric study of dc O_2 discharges at 0.4 torr, though the weakly bound ion could have dissociated in the large electric field at the sampling orifice as Schmidt²¹ suggests for N_4^+ in his mass-spectrometric study of nitrogen ions. The above mechanism does have the desirable property that it is easily quenched by small amounts of added gases such as N_2 or H_2 which are capable of transforming the oxygen ions into more stable ions such as NO^+ or H_3O^+ , but it is unlikely to be important here.

The process $O^- + O \rightarrow O_2 + e$ is known to be fast ($k = 1.5 \times 10^{-10}$) and it should follow the dissociative attachment step $e + O_2 \rightarrow O^- + O$ which has a threshold of 4.5 ev and a low maximum near 7 ev. Insofar as O^- is formed mainly by this reaction and removed by its reverse, and the concentrations of electrons and ions are very much lower than those of neutral species, these steps leave $[O]$ unchanged.

If the above large excitation-dissociation rates are approximately correct, the O-atom yield, as the H-atom yield in the preceding section, is principally controlled by surface recombination in the discharge. The smallest calculated $[O]_{ss}$ ($\gamma = 1$) is about 0.04 torr, 4% mole fraction, considerably larger than experimental values for pure O_2 . A possible explanation of this discrepancy may lie in the surface properties immediately downstream from the discharge region. Active discharges have a sharp boundary as shown by their light emission, because electron loss processes are very fast. The corresponding transition of the surface from a region where γ is near unity to one where it is less than 10^{-4} is likely to be more gradual, and would provide a region in which large, highly localized surface loss terms could quickly reduce the atom concentration.

Experimentally, large catalytic effects by N_2 , NO, or H_2 in the production of O-atoms in microwave discharges have been reported.²² Very pure oxygen gave only 0.6% atoms (still lower yields of 0.3% were later obtained), but small additions (0.01 to 0.05%) of N_2 , N_2O , or NO produced O-atoms at the rate of 40 to 45 per added N, and similar additions of H_2 produced 160 to 200 O-atoms per added H_2 . In terms of the present interpretation, the large catalytic effect may be understandable for H_2 additions as due to H_2O wall effects, but less so for nitrogen compounds which should not be strongly adsorbed at the surface. Conceivably, NO^+ or NO_2^+ , strong Lewis acids, may be involved in poisoning the surface. Thus, our understanding of O_2 discharges is still in an unsatisfactory state. Further experiments are required in which particular attention should be given to the condition and characterization of the surface as well as to the immediate downstream region.

III. 4. Nitrogen Discharges.

The great complexity of "active nitrogen" is probably due to its larger cross sections for vibrational excitation and to the existence of metastable electronically excited states below the dissociation limit of ground-state N_2 . Consequently, extensive vibrational excitation persists for times much longer than those spent in the discharge zone, and chemiionization is observed in regions such as the "pink glow" well downstream of the discharge. The absence of the lowest triplet state, $A, {}^3\Sigma_u^+$, in active nitrogen²³ containing N-atoms indicates that these excited molecules are very efficiently quenched by N, and that vibrationally highly excited ground-state molecules are the principal carriers of excitation to the downstream region. Engelhardt, Phelps, and Risk²⁴ have determined the relevant elastic and inelastic electron collision cross sections. Some of the electronically excited states above the dissociation limit do not lead to predissociation, and therefore only the state with

threshold energy of 14V was used in the estimate of dissociation. Assuming an average electron energy, $\epsilon_k = 3$ ev, and a maxwellian distribution, one obtains an effective dissociation rate constant, k_d , of 3×10^{-10} (60 torr/sec) and a corresponding ionization rate constant, k_i , of 6×10^{-11} . The latter is larger (6 torr/sec) than the corresponding ambipolar diffusion loss term (0.5 to 1 torr/sec). The more realistic calculation by Dr. Phelps which simultaneously fits ϵ_k , E/N , and the known cross sections to make the ambipolar diffusion loss equal the rate of ionization gave $\epsilon_k = 2.2$ ev, $E/N = 1.2 \times 10^{-15}$ V cm²/molecule, $k_d = 3 \times 10^{-11}$ (6 torr/sec), and $k_i = 3 \times 10^{-12}$. The dissociation rate is very much lower than that of H₂ or O₂ and properly reflects the difficulty of producing extensive dissociation of N₂ in glow discharges. No other source terms of comparable magnitude are available. The principal loss processes include atom recombination at the surface which can be set equal to those of oxygen, because the molecular velocities are similar. The catalytic atom loss mechanism by $N_4^+ + N \rightarrow N_3^+ + N_2$, $N_3^+ + N \rightarrow N_2^+ + N_2$, and $N_2^+ + N_2 \rightarrow N_4^+$ has been suggested by Young et al.²⁵ The binding energy of N_4^+ is about 0.5 ev²⁶. but its direct, bimolecular formation is reported to be very slow²⁷. It must be expected that the association of such a simple complex will not be in its second-order (high pressure) limit at 1 torr pressure, and the catalytic loss process then becomes inoperative, as its rate is limited by a relatively slow three-body reaction. The balance of the main production and loss terms here predicts a minimum $[N]_{ss}$ of 0.1% when γ is near unity and the recombination in the close post-discharge region is neglected. When γ is sufficiently small to make $[N]_{ss}$ about 20 to 50 times larger, the corresponding surface recombination rate constant, k_s , is relatively small (100 sec⁻¹) and the half life for attaining steady state may become longer than the residence time so that dissociation becomes source-controlled. This has been observed in recent experiments in our laboratory where two microwave discharges in series in rapidly pumped N₂ at 7 torr produced approximately twice the $[N]$ of each one operating alone.

Experimentally, there is abundant evidence for "catalytic" effects as summarized by Young et al.²⁸ who studied the effectiveness of O_2 , NO, and SF_6 added either before or immediately after a microwave discharge in highly purified, flowing N_2 . All three gases were "catalytic" when added before, but only NO after the discharge, and SF_6 added before "produced" 230 N-atoms per SF_6 molecule. The ESR method employed may give erroneous results, however.²⁹ At the present writing, these effects, as the similar ones in H_2 or O_2 , can only be understood in terms of surface effects in the discharge. In addition, long-lived vibrational excitation is probably responsible for downstream "pink glow" chemiionization effects. The electron impact cross sections are largest for the production of ground-state N_2 with relatively little vibrational excitation²⁹ ($V = 1$ to 4). If these states are extensively populated, the gas will leave the discharge with vibrational energy corresponding to a temperature of 5,000 to 10,000°K, but in a non-equilibrium distribution, lacking its proper complement of highly energetic molecules. These will be formed by vibration-vibration energy transfer which may be relatively slow at the higher levels where the anharmonicity is large.

IV. DISCHARGE CHEMISTRY IN MORE COMPLICATED SYSTEMS.

Although this is the area of greatest interest to most chemists, the necessary fundamental information is mostly lacking. Data on some triatomic molecules such as CO_2 ¹⁹ and H_2O ³¹ have been analyzed. Their active discharges will also contain diatomic molecules such as CO, O_2 , OH, or H_2 as well as the free atoms. This means that reactions between the various neutral species must also be considered. These may be much slower than the electron impact processes and may require long residence times in the discharge to reach their steady state. The approach to full steady state may therefore be characterized by several time constants, very short ones for ionization and direct excitation

or dissociation, and various superimposed longer ones due to reactions of neutral species requiring an energy of activation (e.g. hydrogen abstraction from hydrocarbons which often has an E of 7 to 10 kcal/mole).

Glow discharges in water vapor are a good example of the chemical complexity of simple polyatomic systems. Their chemistry was long misrepresented on the assumption that dissociation to H and OH was the principal discharge reaction and that their recombination could be measured downstream. Space-resolved line absorption experiments on OH in a fast-flow steady-state system³² showed however, that negligible amounts of OH were present a few milliseconds downstream of the discharge, but that a little OH was produced further downstream by slow reactions such as $H + O_2 + M \rightarrow HO_2 + M$ and $H + HO_2 \rightarrow 2 OH$. Thus the discharge is an excellent source of H-atoms, but the further excitation-dissociation of OH is apparently so rapid that O-atoms are also formed, and the very fast reaction $O + OH \rightarrow O_2 + H$ accounts for the major discharge products which are H-atoms and O_2 . When the dissociation of OH in the discharge is insufficient to produce the O-atoms needed in the above reaction, OH may leave the discharge, but will react rapidly by $2 OH \rightarrow H_2O + O$ and $OH + O \rightarrow O_2 + H$ for an overall stoichiometry of $3 OH \rightarrow H_2O + O_2 + H$. Should OH be extensively dissociated in the discharge as appears to be the case at pressures below 0.1 torr, O-atoms will persist, and the overall discharge products will consist of varying amounts of H, O, and O_2 , with H always in great excess. It is clear from this discussion that the primary electron energy and cross section data obtained from transport properties in pure H_2O are much less applicable in determining principal discharge products and their yields. The ionization threshold and cross sections in H_2O are very similar to those in O_2 . The excitation-dissociation cross sections have higher thresholds (12.0 and 12.6 eV), but rise more sharply with increasing electron energy, so that one would expect the primary ionization rate to be equal to that in O_2 , and the primary dissociation rate to be a little lower if ϵ_k is

comparable. All ions will be extensively hydrated which should increase the rate constants of many bimolecular ion-molecule reactions and make it possible for association reactions to take place by simple two-body processes.

In conclusion, the varied aspects of glow discharge chemistry should be summarized once more. In the case of moderately complex reactants, one should have knowledge of many things in order to progress from a cookbook level to one of (partial) understanding: (a) Electron impact ionization and dissociation rates of reactants and other major species; (b) Surface recombination rates in the discharge; (c) Ion-molecule reaction rates involving major neutral species; (d) neutral-neutral reaction rates and their temperature dependences in and out of the discharge. Much of the necessary information for (a), (c), and (d) is becoming available for many systems. The role of the surface, however, is little understood for electrically neutral reactants, even less so for charged species, and seems to be the present bottleneck.

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